Field emission of zinc oxide nanowires grown on carbon cloth

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An extremely low operating electric field has been achieved on zinc oxide (ZnO) nanowire field emitters grown on carbon cloth. Thermal vaporization and condensation was used to grow the nanowires from a mixture source of ZnO and graphite powders in a tube furnace. An emission current density of 1 mA/cm² was obtained at an operating electric field of 0.7 V/μm. Such low field results from an extremely high field enhancement factor of 4.11 × 10⁴ due to a combined effect of the high intrinsic aspect ratio of ZnO nanowires and the woven geometry of carbon cloth. © 2004 American Institute of Physics. [DOI: 10.1063/1.1784543]

Field emission is one of the many applications of one-dimensional nanostructured materials including nanotubes, nanowires, and nanorods. It is of great commercial interest in vacuum microelectronic devices such as field emission displays, x-ray sources, microwave devices, etc. Among various one-dimensional nanostructured materials, carbon nanotubes have attracted extensive efforts. However, few studies have been carried out on field emission of other nanostructured materials.

Recently, several groups have investigated the field emission of various zinc oxide (ZnO) nanowires such as well-aligned, randomly oriented, tetrapod-like, and gallium-doped ZnO nanowires. In addition to the wide direct band gap and large exciton binding energy of ZnO nanowires, the thermal stability and oxidation resistance make it a good candidate as a field emitter. Among the reported field emission results of ZnO nanowires, the lowest electric field of 4.5 V/μm as listed in Table I is required to obtain an emission current density of 1 mA/cm², which is the minimum emission current density required to produce the luminance of 300 cd/m² from VGA FED with typical high-voltage phosphor screen efficacy of 9 lm/W.

In order to achieve lower electric field (below 4 V/μm), we used carbon cloth as substrate on which ZnO nanowires were grown because superior field emission has been observed from the carbon nanotubes grown on carbon cloth. Carbon cloth is a woven textile material consisting of carbon fibers oriented in two directions, as shown in Fig. 1. The carbon fibers of about 10 μm in diameter in carbon cloth have good conductivity. Due to the woven nature of carbon cloth, it provides additional field enhancement to the intrinsic field enhancement of ZnO nanowires due to their high aspect ratio.

The ZnO nanowires were synthesized on carbon cloth by vaporization and condensation employing the same method reported before. Briefly, a mixture source of ZnO powder (Alfa Aesar, 99.9%) and graphite powder (Alfa Aesar, 99.9%) was loaded at the higher temperature zone and the carbon cloth was placed in the lower temperature zone of a horizontal tube furnace. The furnace was heated up to 1100 °C at a rate of 50 °C/min and kept for 25 min with a pressure of 2 Torr maintained by a constant argon gas flow of 50 sccm. The temperature where the carbon cloth was placed was 725–750 °C. Since no catalysts were used, the ZnO nanowires were grown following the vapor–solid or the self-catalyzing growth mechanism. In this process, the zinc and zinc sub-oxide vapor were produced by carbothermal reduction and subsequently condensed in the lower temperature zone as the catalyst on which ZnO nanowires were grown.

Figure 2 shows the scanning electron microscope (SEM) images of the ZnO nanowires grown on carbon cloth. The nanowires are of about 5–10 μm in length as shown in Fig. 2(b) and of about 50 nm in diameter as shown in Fig. 2(c). Clearly, the surface of the carbon fibers is partially covered by ZnO nanowires. The low density due to the partial coverage is beneficial to field enhancement factor because it reduces the screening effect usually observed in the high density nanotube and nanowire films.

The field emission current of the ZnO nanowires grown on carbon cloth was measured using a simple planar diode configuration. The anode was a molybdenum disk with a diameter of 5 mm, and the gap between the carbon cloth and the anode was 2.5 mm. The vacuum level was kept below 1 × 10⁻⁶ Torr during measurement. The measured current density as a function of the macroscopic electric field is shown in Fig. 3. A turn-on electric field of 0.2 V/μm was obtained at an emission current density of 0.1 μA/cm² (see the inset). A horizontal line at the emission current density of 1 mA/cm² was drawn to determine the electric field of 0.7 V/μm, which is much lower than the lowest reported value of ZnO nanowires (see Table I).

<table>
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<tr>
<th>Reference</th>
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TABLE I. The electric field required to obtain emission current density of 1 mA/cm², the field enhancement factor, and the assumed work function for various ZnO nanowires in the literature.

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The Fowler–Nordheim plot for the measured sample is shown in Fig. 4. It is clearly shown that the measured data fit well to the linear relationship given by

$$\log(J/F^2) = \log(A \gamma^2/\varphi) - B\varphi^{3/2}/\gamma F,$$

where $A = 1.54 \times 10^{-6} \text{ A eV V}^{-2}$, $B = 6.83 \times 10^{3} \text{ eV}^{-3/2} \text{ V} \mu\text{m}^{-1}$, $\gamma$ is the field enhancement factor, and $\varphi$ is the work function of emitter material. Assuming $\varphi = 5.3 \text{ eV}$ for ZnO, a field enhancement factor was calculated to be $4.11 \times 10^{4}$ from the slope of the straight line in Fig. 4. It is the highest value ever reported for ZnO nanowires, as listed in Table I. It is even higher than those of the single-wall and multiwall carbon nanotubes films ($\sim 1.1 \times 10^{4}$), single tungsten wire field emitter ($\sim 1.8 \times 10^{4}$), and carbon nanotubes on carbon cloth.

The intrinsic field enhancement factor of an individual nanowire is approximately proportional to the aspect ratio of $l/r$, where $l$ and $r$ are the length and radius of nanowire, respectively. Since the length and radius of ZnO nanowires are $10 \mu\text{m}$ and $25 \text{ nm}$, respectively, the intrinsic field enhancement factor of ZnO nanowires is calculated to be only $4 \times 10^{2}$. Even an exceptionally long length of $20 \mu\text{m}$ and small radius of $5 \text{ nm}$ are assumed, the calculated intrinsic field enhancement factor is only $4 \times 10^{3}$, which is an order of magnitude smaller than the experimental value. Therefore, the high field enhancement factor of ZnO nanowires grown on carbon cloth is believed to be the result of a combined effect of the intrinsic geometry of ZnO nanowire and that of carbon cloth. Since the protruding carbon fibers of the carbon cloth have an average radius of $5 \mu\text{m}$ and length in the order of $100 \mu\text{m}$, as shown in Fig. 1, a field enhancement factor of about 100 for the protruding carbon fiber is estimated. This field enhancement of the protruding carbon fiber was further enhanced by the ZnO nanowires by about $4 \times 10^{2}$, leading to a combined field enhancement factor of about $4 \times 10^{4}$, which is similar to the experimental value as measured.

In summary, an electric field of as low as $0.7 \text{ V/\mu m}$ is needed to obtain an emission current density of $1 \text{ mA/cm}^2$ of zinc oxide nanowires grown on carbon cloth. It is believed that the combined field enhancement due to the high intrinsic aspect ratio of ZnO nanowires and the woven geometry of carbon cloth is responsive.

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FIG. 4. The Fowler–Nordheim plot of the field emission current density of ZnO nanowires grown on carbon cloth.